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LECTURE 6

Assembly of independent molecules

So far the description of the interaction between light and matter has been in a very general form, where it was assumed merely that the interaction is local, and in the electric dipolar approximation, where magnetic dipolar and electric quadrupolar interactions (as well as higher order terms) were neglected. The ensemble of molecules has so far no constraints in terms of composition or mutual interaction, and the electric dipolar operator is so far taken for the *whole ensemble of molecules*, rather than as the dipole operator for the individual molecules.
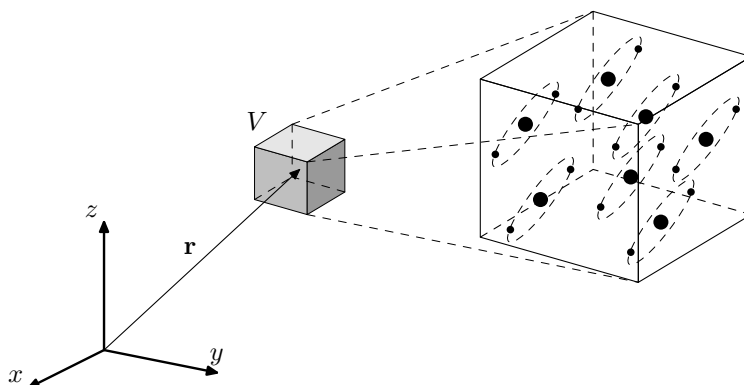

Figure 1. The ensemble of identical, similarly oriented, and mutually independent molecules.

For many practical applications, however, the obtained general form is somewhat inconvenient when it comes to the numerical evaluation of the susceptibilities, since tables of wave functions, transition frequencies and their corresponding electric dipole moments etc. often are tabulated exclusively for the individual molecules themselves. Thus, we will now apply the obtained general theory to an ensemble of identical molecules, making a transition from the wave function and electric dipole operator of the whole ensemble to the wave function and electric dipole operator of the individual molecule, and find an explicit form of the electric susceptibilities in terms of the *quantum mechanical matrix elements of the molecular dipole operator*.

   We will now apply three assumptions of the ensemble of molecules, which introduce a significant simplification to the task of expressing the susceptibilities and macroscopic polarization density in terms of the individual molecular properties:

1. The molecules of the ensemble are all identical.
2. The molecules of the ensemble are mutually non-interacting.
3. The molecules of the ensemble are identically oriented.

   From a wave functional approach, it is straightforward to make the transition from the description of the ensemble down to the molecular level in a strict quantum mechanical perspective (as shown in Butcher and Cotters book). However, from a practical engineering point of view, the results are quite intuitively derived if we make the following observations, which immediately follow from the assumptions listed above:

• The positions of the individual molecules does not affect the electric dipole moment of the whole ensemble in V, if we neglect the mutual interaction between the molecules. (This holds

only if the molecules are neutrally charged, since they otherwise could build up a total electric dipole moment of the ensemble.)

• Since the mutual interaction between the molecules is neglected, we may just as well consider the individual molecules as constituting a set of "sub-ensembles" of the general ensemble picture. In this picture, all quantum mechanical expectation values, involved commutators, matrix elements, etc., should be considered for each subensemble instead, and the macroscopic polarization density will in this case become

$$\mathbf{P}(\mathbf{r},t) = \frac{\left\{\begin{array}{c}\text{the number of molecules}\\ \text{within the volume } V\end{array}\right\} \times \left\{\begin{array}{c}\text{the expectation value of the}\\ \text{molecular dipole operator}\end{array}\right\}}{\{\text{the volume } V\}}.$$
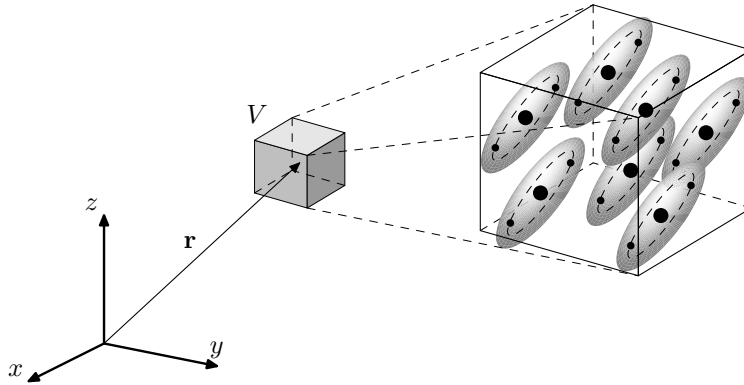

Figure 2. The general ensemble seen as an ensemble of identical mono-molecular sub-ensembles.

Assuming there are M mutually non-interacting and similarly oriented molecules in the volume V, the macroscopic polarization density of the medium can be written as

$$\mathbf{P}(\mathbf{r},t) = \frac{1}{V}\langle\hat{\mathbf{Q}}\rangle = \frac{1}{V}\langle\underbrace{-e\sum_j \hat{\mathbf{r}}_j}_{\text{electrons}} + \underbrace{e\sum_k Z_k\hat{\mathbf{r}}_k}_{\text{nuclei}}\rangle$$

$$= \{\text{arrange terms as sum over the molecules of the ensemble}\}$$

$$= \frac{1}{V}\langle\underbrace{\sum_{m=1}^{M}\Big(\underbrace{-e\sum_j \hat{\mathbf{r}}_j^{(m)}}_{\text{electrons}} + \underbrace{e\sum_k Z_k^{(m)}\hat{\mathbf{r}}_k^{(m)}}_{\text{nuclei}}\Big)}_{\substack{\text{molecular elec. dipole operator, } e\hat{\mathbf{r}}^{(m)} \\ \text{electric dipole moment of ensemble}}}\rangle$$

$$= \frac{1}{V}\langle\sum_{m=1}^{M} e\hat{\mathbf{r}}^{(m)}\rangle$$

$$= \{\text{the molecules are mutually noninteracting}\}$$

$$= \frac{1}{V}\sum_{m=1}^{M}\langle e\hat{\mathbf{r}}^{(m)}\rangle$$

$$= \{\text{the molecules are identical and similarly oriented}\}$$

$$= \frac{1}{V}\sum_{m=1}^{M}\langle e\hat{\mathbf{r}}\rangle$$

$$= N\langle e\hat{\mathbf{r}}\rangle$$

where $N = M/V$ is the number of molecules per unit volume, and

$$\langle e\hat{\mathbf{r}} \rangle = \text{Tr}[\hat{\varrho}(t)e\hat{\mathbf{r}}]$$

is the expectation value of the *mono-molecular* electric dipole operator, with $\hat{\varrho}(t)$ (that is to say, $\hat{\rho}(t)$ with a "kink"[1] to indicate the difference to the density operator of the general ensemble) is the molecular density operator. Notice that the form $\mathbf{P}(\mathbf{r},t) = N\langle e\hat{\mathbf{r}} \rangle$ is identical to the previous form for the general ensemble, though with the factor $1/V$ replaced by $N = M/V$, and with the electric dipole operator $\hat{Q}_\alpha$ of the ensemble replaced by the molecular dipole moment operator $e\hat{r}_\alpha$.

When making this transition, the condition that the molecules are mutually independent is simply a statement that we *locally* assume the superposition principle of the properties of the molecules (wave functions, electric dipole moments, etc.) to hold.

Going in the limit of non-interacting molecules, we may picture the situation as in Fig. 2, with each molecule defining a sub-ensemble, which we are free to choose as our "small volume" of charged particles. As long as we do not make any claim to determine the exact individual positions of the charged particles together with their respective momentum (or any other pair of canonical variables which would violate the Heisenberg uncertainty relation), this is a perfectly valid picture, which provides the statistical expectation values of any observable property of the medium as M/V times the average statistical molecular observations.

The previously described operators of a general ensemble of charged particles should in this case be replaced by their corresponding mono-molecular equivalents, as listed in the following table.

General ensemble		Molecular representation	
$\hat{Q}_\mu$	$\rightarrow$	$e\hat{r}_\mu$	(Electric dipole operator)
$\hat{\rho}_0$	$\rightarrow$	$\hat{\varrho}_0$	(Density operator of thermal equilibrium)
$\hat{\rho}_n(t)$	$\rightarrow$	$\hat{\varrho}_n(t)$	(nth order term of density operator)
$\hat{H}_0$	$\rightarrow$	$\hat{\mathcal{H}}_0$	(Hamiltonian of thermal equilibrium)
$1/V$	$\rightarrow$	$N = M/V$	(Number density of molecules)
$\rho_0(a)$	$\rightarrow$	$\varrho_0(a)$	(Molecular population density at state $|a\rangle$)

Whenever an operator is expressed in the interaction picture, we should keep in mind that the corresponding time development operators $\hat{U}_0(t)$, which originally were expressed in terms of the thermal equilibrium Hamiltonian $\hat{H}_0$ of the ensemble, now should be expressed in terms of the mono-molecular thermal equilibrium Hamiltonian $\hat{\mathcal{H}}_0$.

The matrix elements of the mono-molecular electric dipole operator, taken in the interaction picture, become

$$
\begin{aligned}
\langle a|e\hat{r}_\alpha(t)|b\rangle &= \langle a|\hat{U}_0(-t)e\hat{r}_\alpha\hat{U}_0(t)|b\rangle \\
&= \{\text{the closure principle, B.\&C. Eq. (3.11)}, [\hat{O}\hat{O}']_{ab} = \sum_k O_{ak}O_{kb}\} \\
&= \sum_k \sum_l \langle a|\hat{U}_0(-t)|k\rangle\langle k|e\hat{r}_\alpha|l\rangle\langle l|\hat{U}_0(t)|b\rangle \\
&= \{\text{energy representation, B.\&C. Eq. (4.54)}, [\hat{U}_0(t)]_{ab} = \exp(-i\mathbb{E}_a t/\hbar)\delta_{ab}\} \quad (3) \\
&= \sum_k \sum_l \exp(-i\mathbb{E}_a(-t)/\hbar)\delta_{ak}\langle k|e\hat{r}_\alpha|l\rangle\exp(-i\mathbb{E}_l t/\hbar)\delta_{lb} \\
&= \langle a|e\hat{r}_\alpha|b\rangle\exp[i\underbrace{(\mathbb{E}_a - \mathbb{E}_b)t/\hbar}_{\equiv\Omega_{ab}t}] \\
&= \langle a|e\hat{r}_\alpha|b\rangle\exp(i\Omega_{ab}t),
\end{aligned}
$$

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[1] **kink** *n.* **1.** a sharp twist or bend in a wire, rope, hair, etc. [*Collins Concise Dictionary*, Harper-Collins (1995)].

where $\Omega_{ab} = (\mathbb{E}_a - \mathbb{E}_b)/\hbar$ is the molecular transition frequency between the molecular states $|a\rangle$ and $|b\rangle$. We may thus, at least in some sense, interpret the interaction picture for the matrix elements of the molecular operators as an out-separation of the naturally occurring transition frequencies associated with a change from state $|a\rangle$ to $|b\rangle$ of the molecule.

First order electric susceptibility

From the general form of the first order (linear) electric susceptibility, as derived in the previous lecture, one obtains

$$\chi^{(1)}_{\mu\alpha}(-\omega;\omega) = -\frac{N}{\varepsilon_0 i\hbar} \int_{-\infty}^{0} \mathrm{Tr}\{\hat{\varrho}_0[e\hat{r}_\mu, e\hat{r}_\alpha(\tau)]\} \exp(-i\omega\tau)\,d\tau$$

$$= -\frac{Ne^2}{\varepsilon_0 i\hbar} \int_{-\infty}^{0} \sum_a \langle a|\hat{\varrho}_0(\hat{r}_\mu \hat{r}_\alpha(\tau) - \hat{r}_\alpha(\tau)\hat{r}_\mu)|a\rangle \exp(-i\omega\tau)\,d\tau$$

$$= \{\text{the closure principle}\}$$

$$= -\frac{Ne^2}{\varepsilon_0 i\hbar} \int_{-\infty}^{0} \sum_a \sum_k \langle a|\hat{\varrho}_0|k\rangle\langle k|\hat{r}_\mu \hat{r}_\alpha(\tau) - \hat{r}_\alpha(\tau)\hat{r}_\mu|a\rangle \exp(-i\omega\tau)\,d\tau$$

$$= \{\text{use that } \langle a|\hat{\varrho}_0|k\rangle = \varrho_0(a)\delta_{ak}\}$$

$$= -\frac{Ne^2}{\varepsilon_0 i\hbar} \int_{-\infty}^{0} \sum_a \varrho_0(a)\big[\langle a|\hat{r}_\mu \hat{r}_\alpha(\tau)|a\rangle - \langle a|\hat{r}_\alpha(\tau)\hat{r}_\mu|a\rangle\big] \exp(-i\omega\tau)\,d\tau$$

$$= \{\text{the closure principle again}\}$$

$$= -\frac{Ne^2}{\varepsilon_0 i\hbar} \int_{-\infty}^{0} \sum_a \varrho_0(a) \sum_b \big[\langle a|\hat{r}_\mu|b\rangle\langle b|\hat{r}_\alpha(\tau)|a\rangle - \langle a|\hat{r}_\alpha(\tau)|b\rangle\langle b|\hat{r}_\mu|a\rangle\big] \exp(-i\omega\tau)\,d\tau$$

$$= \{\text{Use results of Eq. (3) and shorthand notation } \langle a|\hat{r}_\alpha|b\rangle = r_{ab}^\alpha\}$$

$$= -\frac{Ne^2}{\varepsilon_0 i\hbar} \sum_a \varrho_0(a) \sum_b \int_{-\infty}^{0} \big[r_{ab}^\mu r_{ba}^\alpha \exp(i\Omega_{ba}\tau) - r_{ab}^\alpha r_{ba}^\mu \exp(-i\Omega_{ba}\tau)\big] \exp(-i\omega\tau)\,d\tau$$

$$= \{\text{evaluate integral } \int_{-\infty}^{0} \exp(iC\tau)\,d\tau \to 1/(iC)\}$$

$$= -\frac{Ne^2}{\varepsilon_0 i\hbar} \sum_a \varrho_0(a) \sum_b \left[\frac{r_{ab}^\mu r_{ba}^\alpha}{i(\Omega_{ba}-\omega)} - \frac{r_{ab}^\alpha r_{ba}^\mu}{-i(\Omega_{ba}+\omega)}\right]$$

$$= \frac{Ne^2}{\varepsilon_0 \hbar} \sum_a \varrho_0(a) \sum_b \left(\frac{r_{ab}^\mu r_{ba}^\alpha}{\Omega_{ba}-\omega} + \frac{r_{ab}^\alpha r_{ba}^\mu}{\Omega_{ba}+\omega}\right).$$

This result, which was derived entirely under the assumption that all resonances of the medium are located far away from the angular frequency of the light, possesses a new type of symmetry, which can be seen if we make the interchange

$$(-\omega, \mu) \rightleftharpoons (\omega, \alpha),$$

which by using the above result for the linear susceptibility gives

$$\chi^{(1)}_{\alpha\mu}(\omega;-\omega) = \frac{Ne^2}{\varepsilon_0 \hbar} \sum_a \varrho_0(a) \sum_b \left(\frac{r_{ab}^\alpha r_{ba}^\mu}{\Omega_{ba}+\omega} + \frac{r_{ab}^\mu r_{ba}^\alpha}{\Omega_{ba}-\omega}\right)$$

$$= \{\text{change order of appearance of the terms}\}$$

$$= \frac{Ne^2}{\varepsilon_0 \hbar} \sum_a \varrho_0(a) \sum_b \left(\frac{r_{ab}^\mu r_{ba}^\alpha}{\Omega_{ba}-\omega} + \frac{r_{ab}^\alpha r_{ba}^\mu}{\Omega_{ba}+\omega}\right)$$

$$= \chi^{(1)}_{\mu\alpha}(-\omega;\omega),$$

which is a signature of the *overall permutation symmetry* that applies to nonresonant interactions. With this result, the reason for the peculiar notation with "$(-\omega;\omega)$" should be all clear, namely

that it serves as an explicit way of notation of the overall permutation symmetry, whenever it applies.

It should be noticed that while intrinsic permutation symmetry is a general property that solely applies to nonlinear optical interactions, the overall permutation symmetry applies to linear interactions as well.

Second order electric susceptibility

In similar to the linear electric susceptibility, starting from the general form of the second order (quadratic) electric susceptibility, one obtains

$$\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma;\omega_1,\omega_2)$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\int_{-\infty}^0\int_{-\infty}^{\tau_1}\mathrm{Tr}\{\hat{\varrho}_0[[\hat{r}_\mu,\hat{r}_\alpha(\tau_1)],\hat{r}_\beta(\tau_2)]\}\exp[-i(\omega_1\tau_1+\omega_2\tau_2)]\,d\tau_2\,d\tau_1$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\int_{-\infty}^0\int_{-\infty}^{\tau_1}\sum_a\langle a|\hat{\varrho}_0[\underbrace{[\hat{r}_\mu,\hat{r}_\alpha(\tau_1)]}_{\hat{r}_\mu\hat{r}_\alpha(\tau_1)-\hat{r}_\alpha(\tau_1)\hat{r}_\mu},\hat{r}_\beta(\tau_2)]|a\rangle\exp[-i(\omega_1\tau_1+\omega_2\tau_2)]\,d\tau_2\,d\tau_1$$

$$= \{\text{expand the commutator}\}$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\int_{-\infty}^0\int_{-\infty}^{\tau_1}\sum_a\Big(\langle a|\hat{\varrho}_0\hat{r}_\mu\hat{r}_\alpha(\tau_1)\hat{r}_\beta(\tau_2)|a\rangle-\langle a|\hat{\varrho}_0\hat{r}_\alpha(\tau_1)\hat{r}_\mu\hat{r}_\beta(\tau_2)|a\rangle$$

$$-\langle a|\hat{\varrho}_0\hat{r}_\beta(\tau_2)\hat{r}_\mu\hat{r}_\alpha(\tau_1)|a\rangle+\langle a|\hat{\varrho}_0\hat{r}_\beta(\tau_2)\hat{r}_\alpha(\tau_1)\hat{r}_\mu|a\rangle\Big)\exp[-i(\omega_1\tau_1+\omega_2\tau_2)]\,d\tau_2\,d\tau_1$$

$$= \{\text{apply the closure principle and Eq. (3)}\}$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\int_{-\infty}^0\int_{-\infty}^{\tau_1}\sum_a\sum_k\sum_b\sum_c\Big(\langle a|\hat{\varrho}_0|k\rangle\langle k|\hat{r}_\mu|b\rangle\langle b|\hat{r}_\alpha(\tau_1)|b\rangle\langle c|\hat{r}_\beta(\tau_2)|a\rangle$$

$$-\langle a|\hat{\varrho}_0|k\rangle\langle k|\hat{r}_\alpha(\tau_1)|b\rangle\langle b|\hat{r}_\mu|c\rangle\langle c|\hat{r}_\beta(\tau_2)|a\rangle$$

$$-\langle a|\hat{\varrho}_0|k\rangle\langle k|\hat{r}_\beta(\tau_2)|b\rangle\langle b|\hat{r}_\mu|c\rangle\langle c|\hat{r}_\alpha(\tau_1)|a\rangle$$

$$+\langle a|\hat{\varrho}_0|k\rangle\langle k|\hat{r}_\beta(\tau_2)|b\rangle\langle b|\hat{r}_\alpha(\tau_1)|c\rangle\langle c|\hat{r}_\mu|a\rangle\Big)\exp[-i(\omega_1\tau_1+\omega_2\tau_2)]\,d\tau_2\,d\tau_1$$

$$= \{\text{use that }\langle a|\hat{\varrho}_0|k\rangle=\varrho_0(a)\delta_{ak}\text{ and apply Eq. (3)}\}$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\sum_a\varrho_0(a)\sum_b\sum_c\int_{-\infty}^0\int_{-\infty}^{\tau_1}\Big\{r_{ab}^\mu r_{bc}^\alpha r_{ca}^\beta\exp[i(\Omega_{bc}\tau_1+\Omega_{ca}\tau_2)]$$

$$-r_{ab}^\alpha r_{bc}^\mu r_{ca}^\beta\exp[i(\Omega_{ab}\tau_1+\Omega_{ca}\tau_2)]-r_{ab}^\beta r_{bc}^\mu r_{ca}^\alpha\exp[i(\Omega_{ca}\tau_1+\Omega_{ab}\tau_2)]$$

$$+r_{ab}^\beta r_{bc}^\alpha r_{ca}^\mu\exp[i(\Omega_{bc}\tau_1+\Omega_{ab}\tau_2)]\Big\}\exp[-i(\omega_1\tau_1+\omega_2\tau_2)]\,d\tau_2\,d\tau_1$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\sum_a\varrho_0(a)\sum_b\sum_c\int_{-\infty}^0\Big\{\frac{r_{ab}^\mu r_{bc}^\alpha r_{ca}^\beta}{i(\Omega_{ca}-\omega_2)}\exp[i\underbrace{(\Omega_{bc}+\Omega_{ca})}_{=\Omega_{ba}}\tau_1]$$

$$-\frac{r_{ab}^\alpha r_{bc}^\mu r_{ca}^\beta}{i(\Omega_{ca}-\omega_2)}\exp[i\underbrace{(\Omega_{ab}+\Omega_{ca})}_{=\Omega_{cb}}\tau_1]-\frac{r_{ab}^\beta r_{bc}^\mu r_{ca}^\alpha}{i(\Omega_{ab}-\omega_2)}\exp[i\underbrace{(\Omega_{ca}+\Omega_{ab})}_{=\Omega_{cb}}\tau_1)]$$

$$+\frac{r_{ab}^\beta r_{bc}^\alpha r_{ca}^\mu}{i(\Omega_{ab}-\omega_2)}\exp[i\underbrace{(\Omega_{bc}+\Omega_{ab})}_{=-\Omega_{ca}}\tau_1]\Big\}\exp[-i\underbrace{(\omega_1+\omega_2)}_{=\omega_\sigma}\tau_1]\,d\tau_1$$

$$= \frac{Ne^3}{\varepsilon_0(i\hbar)^2}\frac{1}{2!}\mathbf{S}\sum_a\varrho_0(a)\sum_b\sum_c\Big\{-\frac{r_{ab}^\mu r_{bc}^\alpha r_{ca}^\beta}{(\Omega_{ca}-\omega_2)(\Omega_{ba}-\omega_\sigma)}+\frac{r_{ab}^\alpha r_{bc}^\mu r_{ca}^\beta}{(\Omega_{ca}-\omega_2)(\Omega_{cb}-\omega_\sigma)}$$

$$+\frac{r_{ab}^\beta r_{bc}^\mu r_{ca}^\alpha}{(\Omega_{ab}-\omega_2)(\Omega_{cb}-\omega_\sigma)}-\frac{r_{ab}^\beta r_{bc}^\alpha r_{ca}^\mu}{(\Omega_{ab}-\omega_2)(-\Omega_{ca}-\omega_\sigma)}\Big\}$$

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$$= \frac{Ne^3}{\varepsilon_0 \hbar^2} \frac{1}{2!} \mathbf{S} \sum_a \varrho_0(a) \sum_b \sum_c \left\{ \frac{r_{ab}^{\mu} r_{bc}^{\alpha} r_{ca}^{\beta}}{(\Omega_{ac} + \omega_2)(\Omega_{ab} + \omega_\sigma)} - \frac{r_{ab}^{\alpha} r_{bc}^{\mu} r_{ca}^{\beta}}{(\Omega_{ac} + \omega_2)(\Omega_{bc} + \omega_\sigma)} \right.$$
$$\left. - \frac{r_{ab}^{\beta} r_{bc}^{\mu} r_{ca}^{\alpha}}{(\Omega_{ba} + \omega_2)(\Omega_{bc} + \omega_\sigma)} + \frac{r_{ab}^{\beta} r_{bc}^{\alpha} r_{ca}^{\mu}}{(\Omega_{ba} + \omega_2)(\Omega_{ca} + \omega_\sigma)} \right\}.$$

Now it is easily seen that if we, for example, interchange

$$(-\omega_\sigma, \mu) \rightleftharpoons (\omega_2, \beta),$$

one obtains

$$\chi^{(2)}_{\beta\alpha\mu}(\omega_2; \omega_1, -\omega_\sigma)$$

$$= \frac{Ne^3}{\varepsilon_0 \hbar^2} \frac{1}{2!} \mathbf{S} \sum_a \varrho_0(a) \sum_b \sum_c \left\{ \frac{r_{ab}^{\beta} r_{bc}^{\alpha} r_{ca}^{\mu}}{(\Omega_{ac} - \omega_\sigma)(\Omega_{ab} - \omega_2)} - \frac{r_{ab}^{\alpha} r_{bc}^{\beta} r_{ca}^{\mu}}{(\Omega_{ac} - \omega_\sigma)(\Omega_{bc} - \omega_2)} \right.$$
$$\left. - \frac{r_{ab}^{\mu} r_{bc}^{\beta} r_{ca}^{\alpha}}{(\Omega_{ba} - \omega_\sigma)(\Omega_{bc} - \omega_2)} + \frac{r_{ab}^{\mu} r_{bc}^{\alpha} r_{ca}^{\beta}}{(\Omega_{ba} - \omega_\sigma)(\Omega_{ca} - \omega_2)} \right\}$$

$$= \{ \text{use } \Omega_{ab} = -\Omega_{ba}, \text{ etc.} \}$$

$$= \frac{Ne^3}{\varepsilon_0 \hbar^2} \frac{1}{2!} \mathbf{S} \sum_a \varrho_0(a) \sum_b \sum_c \left\{ \underbrace{\frac{r_{ab}^{\beta} r_{bc}^{\alpha} r_{ca}^{\mu}}{(\Omega_{ca} + \omega_\sigma)(\Omega_{ba} + \omega_2)}}_{\text{identify 4th term}} - \frac{r_{ab}^{\alpha} r_{bc}^{\beta} r_{ca}^{\mu}}{(\Omega_{ca} + \omega_\sigma)(\Omega_{cb} + \omega_2)} \right.$$
$$\left. - \frac{r_{ab}^{\mu} r_{bc}^{\beta} r_{ca}^{\alpha}}{(\Omega_{ab} + \omega_\sigma)(\Omega_{cb} + \omega_2)} + \underbrace{\frac{r_{ab}^{\mu} r_{bc}^{\alpha} r_{ca}^{\beta}}{(\Omega_{ab} + \omega_\sigma)(\Omega_{ac} + \omega_2)}}_{\text{identify 1st term}} \right\}$$

$$= \{ \text{interchange dummy indices } a \to c \to b \to a \text{ in 2nd term} \}$$
$$= \{ \text{interchange dummy indices } a \to b \to c \to a \text{ in 3rd term} \}$$

$$= \frac{Ne^3}{\varepsilon_0 \hbar^2} \frac{1}{2!} \mathbf{S} \sum_a \varrho_0(a) \sum_b \sum_c \left\{ \underbrace{\frac{r_{ab}^{\beta} r_{bc}^{\alpha} r_{ca}^{\mu}}{(\Omega_{ca} + \omega_\sigma)(\Omega_{ba} + \omega_2)}}_{\text{identify 4th term}} - \underbrace{\frac{r_{ca}^{\alpha} r_{ab}^{\beta} r_{bc}^{\mu}}{(\Omega_{bc} + \omega_\sigma)(\Omega_{ba} + \omega_2)}}_{\text{identify as 3rd term}} \right.$$
$$\left. - \underbrace{\frac{r_{bc}^{\mu} r_{ca}^{\beta} r_{ab}^{\alpha}}{(\Omega_{bc} + \omega_\sigma)(\Omega_{ac} + \omega_2)}}_{\text{identify as 2nd term}} + \underbrace{\frac{r_{ab}^{\mu} r_{bc}^{\alpha} r_{ca}^{\beta}}{(\Omega_{ab} + \omega_\sigma)(\Omega_{ac} + \omega_2)}}_{\text{identify 1st term}} \right\}$$

$$= \chi^{(2)}_{\mu\beta\alpha}(-\omega_\sigma; \omega_1, \omega_2),$$

that is to say, the second order susceptibility is left invariant under any of the $(2+1)! = 6$ possible pairwise permutations of $(-\omega_\sigma, \mu)$, (ω_1, α), and (ω_2, β); this is the *overall permutation symmetry for the second order susceptibility*, and applies whenever the interaction is moved far away from any resonance.

    We recapitulate that when deriving the form of the nonlinear susceptibilities that lead to intrinsic permutation symmetry, either in terms of polarization response functions in time domain or in terms of a mechanical spring model, nothing actually had to be stated regarding the nature of interaction. This is rather different from what we just obtained for the overall permutation symmetry, as being a signature of a nonresonant interaction between the light and matter, and this symmetry cannot (in contrary to the intrinsic permutation symmetry) be expressed unless the origin of interaction is considered.[2]

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[2] It should though be noticed that the derivation of the susceptibilities still may be performed within a mechanical spring model, as long as the resonance frequencies of the oscillator are removed far from the angular frequencies of the present light.